Extended Abstracts of the 2004 International Conference on Solid State Devices and Materials, Tokyo, 2004, pp. 472-473

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Theoretical Study of Chemical Mechanical Polishing of SiO_2 Surface

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1. Introduction

Chemical-mechanical polishing (CMP) has had a long history in optical glass manufacturing processes and other applications for the final finishing of various materials of the purpose of attaining the desired surface [1]. This desired surface is generated by removing materials at the atomic level with the combined effect of mechanical and chemical reactions. The CMP is expected to solve all the problems related to the roughness of the silicon surface such as the aspect ratio, focus depth and so on.

Ceria has been commonly used as an abrasive for glass polishing. It has the fastest polishing rate among those of SnO_2, TiO_2, ZrO_2, Cr_2O_3, Al_2O_3, Y_2O_3, La_2O_3 and so on [2]. Since CeO_2 is softer than SiO_2, it inflicts less damage such as scratches on the SiO_2 film than the other particles mentioned.

Polishing mechanisms have been studied in the field of optical glass for more than 40 years. Hoshino et al. [2] reported the polishing mechanism of SiO_2 films by CeO_2 particles. However, the chemical contribution has not yet been identified. Liang et al. [3] reported the lubricating behavior in chemical mechanical polishing of copper. Their results show that the polishing is predominately by chemical reaction. Also in Shallow Trench Isolation (STI) of SiO_2/ Si_3N_4 by CeO_2 particles, only SiO_2 surface is selectively polished while Si_3N_4 is not polished by CeO_2 particles. These observations make the greater attraction towards the importance of the chemical contribution in CMP processes. Therefore, in order to understand the selective polishing of SiO_2 in STI process and also to improve the polishing efficiency, it is very essential to analyze how the polishing of SiO_2 films by CeO_2 slurry takes place and also to understand the chemical contribution in CMP process.

In our present investigation, we used our own computational chemistry method to study the surface reactions and chemical contribution of SiO_2 in CMP process.

2. Computational Methods

First-principles molecular dynamics method cannot simulate the CMP processes, because it needs huge calculation time. In our present investigation, we employed a novel tight-binding quantum chemical molecular dynamics simulation method “Colors”, which is recently developed by our group. This programme provides an option to simulate the CMP processes due to its over 5,000 times faster calculation speed than the conventional first-principles molecular dynamics programme [4]. Amsterdam density functional programme package (ADF 2000.02) was used to determine the accurate parameters, which are necessary for our Colors programme.

3. Results and Discussion

The calculation of density of states (DOS) was individually calculated for CeO_2 cluster, SiO_2(100) surface and the Si_3N_4(0001) surface. HOMO of SiO_2(100) surface and LUMO of CeO_2 cluster are very close in energy as shown

Table 1 Comparison of HOMO and LUMO energies of CeO_2 cluster, SiO_2(100) and Si_3N_4(0001) .

	HOMO (eV)	LUMO (eV)
CeO_2 cluster	-11.107	-10.951
SiO_2(100)	-10.966	-3.080
Si_3N_4(0001)	-8.106	-7.138

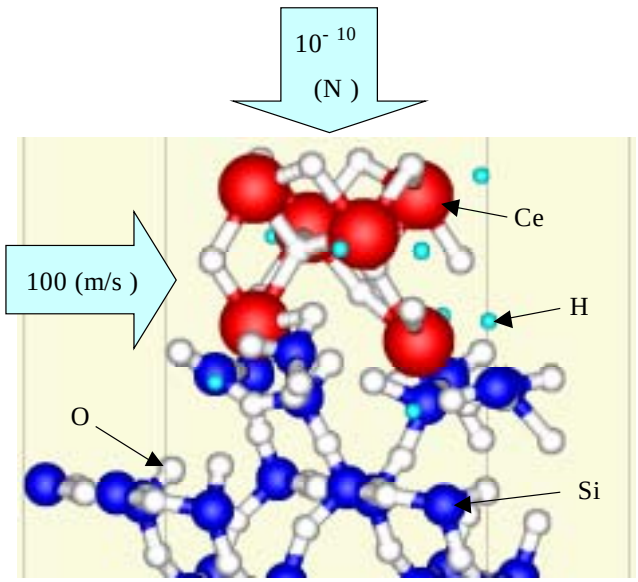

Fig. 1 The model for the simulation of CMP process.

in Table 1, however the HOMO energy of Si_3N_4(0001) surface is very far. Since the HOMO and the LUMO are closer in energy, electron moves from HOMO of the SiO_2 to LUMO of the CeO_2 and a chemical reaction occurs. For this reason Si_3N_4 is not polished in STI process by CeO_2 particles leading to the selective polishing of SiO_2.

Also, quantum chemical molecular dynamics simulation was carried out using the model shown in Fig. 1. For this calculation we used the periodic boundary model and the calculation time is 1000 fs with time interval of 0.2 fs. The temperature of this process was maintained at 300 K. In order to reproduce the actual CMP conditions, the vertical force (to the CeO_2/ SiO_2 interface) of 10^{-10} N and the horizontal force of 100 m/s are applied in this simulation process.

The oxidation-reduction reaction due to the bond dissociation and the bond formation on the surface of SiO_2 was investigated using charge and bond population (Figs. 2 and 3) analysis.

During the CMP simulation, the charge of oxygen atom of SiO_2 surface is increasing and also the charge of Ce atom decreases. So it is well understood that electron transfer occurs from the Oxygen of SiO_2 surface to the Ce atom. Also the bond population of Si – O_{SiO2} decreased. At around 600 fs the bond population of Si – O_{SiO2} becomes zero. So it is clear that the Si – O_{SiO2} bond is broken. Around 800 fs the charge of the Ce atom is decreased rapidly and is due to the reduction of Ce^{4+} to Ce^{3+}. Also the bond population of Ce – O_{CeO2} becomes zero. It indicates that the Ce – O_{CeO2} bond is broken at around 800 fs. After 800 fs a new bond is formed between Si – O_{CeO2} correspondingly, the charge of Ce increases.

From these results, it is clear that during the CMP process of SiO_2 surface by CeO_2 particles, the electron transfer occurs from the oxygen of SiO_2 surface to the Ce atom. So the Ce atom is reduced from the 4+ oxidation state to the 3+ oxidation state. Consequently the Si – O_{SiO2} bond dissociation takes place. In addition, Ce – O_{CeO2} bond dissociation also takes place because of the reduction of Ce atom. Finally a bond is formed between Si – O_{CeO2}. In this way the planarization of the SiO_2 surface is carried out by CeO_2 particles.

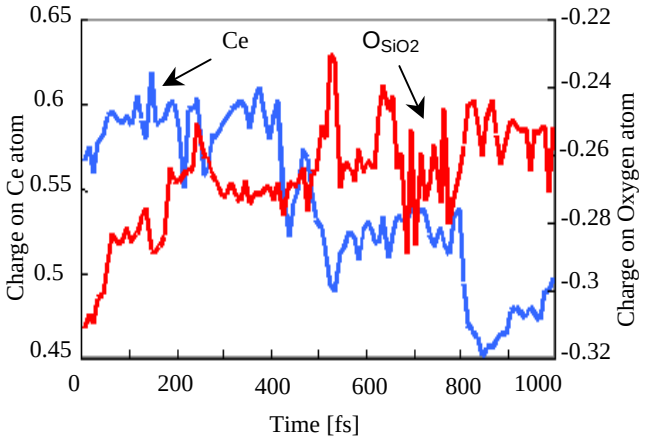

Fig. 2 Charge population on Ce and the oxygen of SiO_2 surface during the simulation of CMP process of SiO_2 surface by CeO_2 particles. Here O_{SiO2} means the oxygen of SiO_2. Around 800 fs the charge of the Ce atom is decreased rapidly and is due to the reduction of Ce^{4+} to Ce^{3+}.

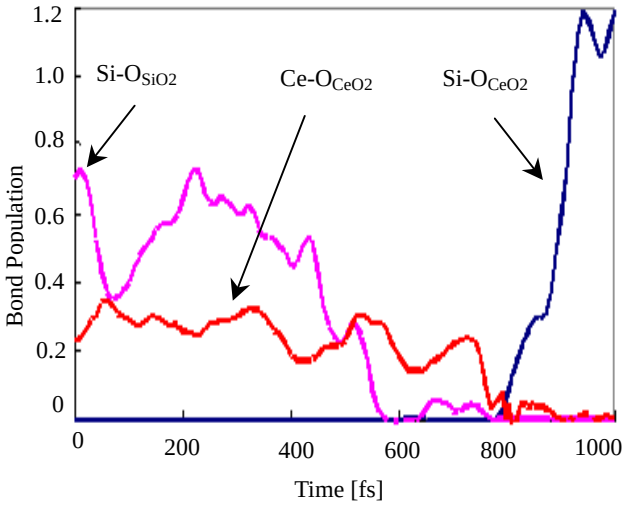

Fig. 3 The bond population analysis during the simulation of CMP process of SiO_2 surface by CeO_2 particles. Here Si-O_{SiO2} means the bond between the Si and the oxygen of SiO_2 and Ce-O_{CeO2} means the bond between the Ce and the oxygen of CeO_2 and Si-O_{CeO2} means the bond between the Si and the oxygen of CeO_2.

4. Conclusions

Chemical mechanical polishing of SiO_2 surface by CeO_2 particles was investigated using our own accelerated quantum chemical molecular dynamics programme. We have successfully clarified the chemical contribution in the CMP processes. We investigated the oxidation-reduction reaction that takes place between the SiO_2 surface and the polishing agent, during the CMP process. We also investigated the formation of a new bond between Si – O_{CeO2}.

References

[1] H.J. Kim, H.Y. Kim, H.D. Jeong, E.S. Lee and Y.J. Shin, Journal of Materials Processing Technology **130-131** (2002) 334-338.

[2] T. Hoshino, Y. Kurata, Y. Terasaki and K. Susa, Journal of Non-Crystalline Solids **283** (2001) 129-136.

[3] H. Liang and G. Helen Xu, Scripta Materialia **46** (2002) 343-347.

[4] T. Yokosuka, H. Kurokawa, S. Takami, M. Kubo, A. Miyamoto and A. Imamura, Jpn. J. Appl. Phys. **41** (2002) 2410.